



STUDY ON FACTORS AFFECTING TO GRAFT COPOLYMERIZATION OF ACRYLAMIDE ON TO “PATANWADI” WOOL

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Abstract:-

The “Patanwadi” Wool was chemically modified by grafting polyacrylamide in a homogeneous aqueous phase by using ceric ammonium nitrate as the initiator. The graft copolymerization of acrylamide onto wool was investigated using ceric ammonium nitrate as the initiator. The effect of initiator concentration, monomer concentration and nitric acid concentration on % G and % GE were studied. The grafted samples were characterized using FTIR and SEM. The water retention values(WRV) have been measured for Grafted wool. From the FTIR data it was ascertained that grafting has occurred considerably. The morphology of the grafted polymer was observed from the SEM pictures. Grafted products improved considerably the physical properties.

Key words: Graft copolymerization, Patanwadi wool, AAM (Acrylamide).

Introduction:

Grafting vinyl monomers onto natural and synthetic polymers is a challenging field of research with unlimited future projection. Last four decades Nayak and co-workers have studied the graft copolymerization of several monomers onto a multitude of natural and synthetic polymers like wool, silk, cellulose, nylon and PET, rubber to enhance their properties using various initiators like hexavalent chromium, quinquivalent vanadium, tetravalent cerium, trivalent manganese, peroxydisulphate and peroxydiphosphate ions¹⁻¹⁵. Wool is a natural protein having polypeptide structure that include a variety of functional groups like hydroxyl, amino, disulphide linkage. Grafting vinyl monomers onto natural and synthetic polymers is a challenging field of research with unlimited future prospects Graft copolymerization is an effective technique used to improve the physical properties of natural fibres. The role of the initiator is very important, as it determines the path of the grafting process. Ceric ion has been extensively used as a redox initiator in graft copolymerization of

vinyl monomers onto wool, cellulose, and starch etc¹⁶⁻²². Tetravalent cerium has been widely used as initiator for vinyl monomers²³⁻²⁸ and graft copolymerization. The popularity of this method arises from its high grafting efficiency compared to other systems²⁹ since the free radicals are formed exclusively on the chains of the substrate. Very little work has been reported on modification of natural wool.

In this paper, we report the grafting of poly(Acrylamide) onto patanwadi wool by using ceric ion initiator in the presence of nitric acid of varying concentration. It was observed that grafting was dependent upon initiator concentration, concentration of monomer and nitric acid used. Concentration of Acrylamide (0.42 mole/lit) was found suitable for efficient grafting of poly(Acrylamide). Beyond this concentration of Acrylamide, grafted wool become sticky even after prolonged washing with solvents. Percentage grafting was found to increase with increase in ceric ion concentration³⁰.

Experimental Method:

Patanwadi wool was washed with distilled water then wash with hot water then purified by extracting with acetone and petroleum ether for **48** hr. The extracted wool was then washed with water and air-dried. Acrylamide was of analytical reagent grade used in whole reaction. Ceric ammonium nitrate (CAN) was of analytical reagent grade and was dissolved in nitric acid of appropriate concentration at the time of addition. Nitrogen was purified by passing through Silica gel, pyragallol and concentrated sulphuric acid.

Graft Copolymerization:

A mixture of 1.0g purified wool and **100** ml water was placed in a three-necked flask and stirred with a magnetic stirrer. The reaction flask was flushed with nitrogen, and the reaction was carried out with bubbling of nitrogen through the reaction mixture. A solution of nitric acid containing a weighted amount of Initiator (CAN) was poured into the reaction mixture. Acrylamide was added gradually under stirring. The reaction was carried out in a water bath at temperatures of 40°C for **3** hrs. The reaction mixture was filtered and washed with water. The residue was freed of homopolymer by extraction with acetone. Percentage grafting and efficiency of grafting were calculated as follows:

$$\% \text{ Grafting} = \frac{\text{weight of poly (Acrylamide) grafted}}{\text{Weight of wool}} \times 100$$

$$\% \text{ Grafting Efficiency} = \frac{\text{Weight of poly(Acrylamide) grafted}}{\text{Weight of Acrylic acid charge}} \times 100$$

RESULTS AND DISCUSSION:

It is apparent from (Table I) that grafting increased with increases in the concentrations of monomer and ceric ion. Similar behavior has been observed with starch and cellulose. However, in the case of wool, the increase in the percentage

grafting is much greater than in starch. Starch and cellulose combine with ceric ion to form a complex which then decomposes, with the generation of active sites on the backbone where graft copolymerization occurs. A similar mechanism holds for wool³¹. Since wool contains a number of functional groups, complex formation with ceric ion is facilitated, and this is why a higher percentage grafting and grafting efficiency were observed in the case of wool. However, it is of interest to note that, in our study, ceric ion alone was not capable of effecting graft copolymerization. With the addition of nitric acid, grafting occurred readily and increased with increasing nitric acid concentration up to 0.20 M (Table I). Beyond this HNO₃ concentration, considerable homopolymer formation occurred, and efficiency of grafting decreased.

Table 1
Grafting of Poly(Acrylamide) onto Wool^a

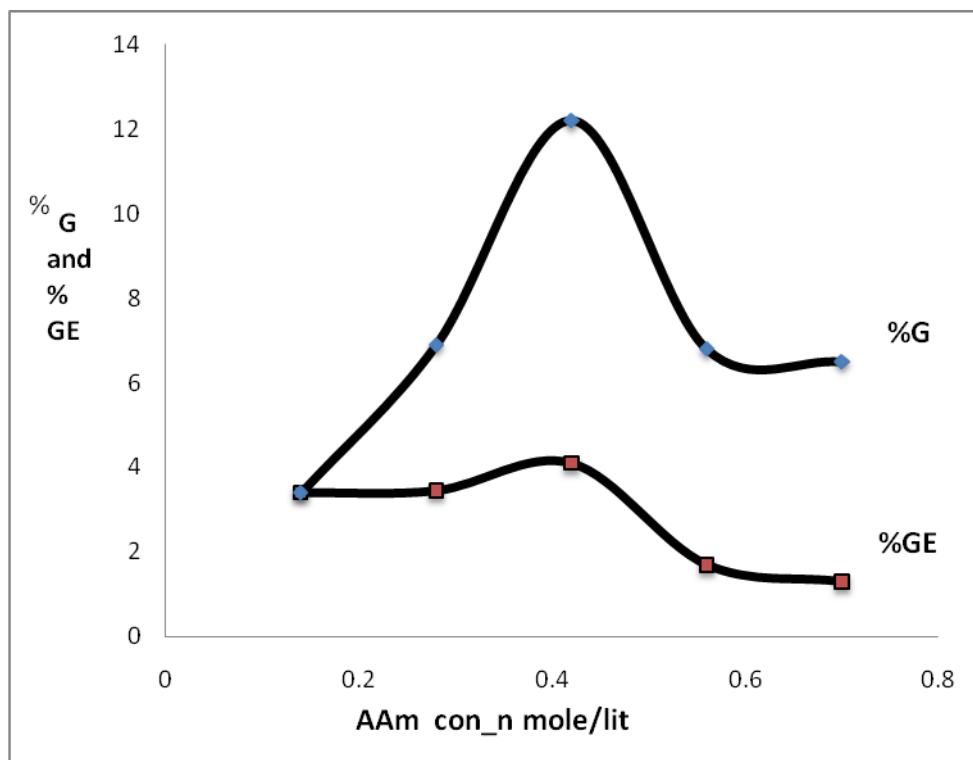
| No. | AAM conc. mole/L | CAN Conc. mole/l | HNO ₃ conc. mole/l | Wool (g) | Temp °c | Time (hrs) | % Grafting | % Grafting Efficiency |
|-----|------------------|------------------|-------------------------------|----------|---------|------------|------------|-----------------------|
| 1 | 0.14 | 0.0075 | 0.1 | 1 | 40 | 3 | 3.4 | 3.40 |
| 2 | 0.28 | 0.0075 | 0.1 | 1 | 40 | 3 | 6.9 | 3.45 |
| 3 | 0.42 | 0.0075 | 0.1 | 1 | 40 | 3 | 12.2 | 4.10 |
| 4 | 0.56 | 0.0075 | 0.1 | 1 | 40 | 3 | 6.8 | 1.70 |
| 5 | 0.70 | 0.0075 | 0.1 | 1 | 40 | 3 | 6.5 | 1.30 |
| 6 | 0.28 | 0.0050 | 0.1 | 1 | 40 | 3 | 5.1 | 2.55 |
| 7 | 0.28 | 0.0075 | 0.1 | 1 | 40 | 3 | 6.9 | 3.45 |
| 8 | 0.28 | 0.0100 | 0.1 | 1 | 40 | 3 | 7.4 | 3.70 |
| 9 | 0.28 | 0.0125 | 0.1 | 1 | 40 | 3 | 7.2 | 3.60 |
| 10 | 0.28 | 0.0150 | 0.1 | 1 | 40 | 3 | 5.8 | 2.90 |
| 11 | 0.28 | 0.0075 | 0.05 | 1 | 40 | 3 | 1.5 | 0.75 |
| 12 | 0.28 | 0.0075 | 0.1 | 1 | 40 | 3 | 6.9 | 3.45 |
| 13 | 0.28 | 0.0075 | 0.15 | 1 | 40 | 3 | 11.6 | 5.80 |
| 14 | 0.28 | 0.0075 | 0.2 | 1 | 40 | 3 | 18.5 | 9.25 |
| 15 | 0.28 | 0.0075 | 0.25 | 1 | 40 | 3 | 11.2 | 5.60 |

In all experiments, 1.0 g of purified wool sample was dispersed in total 100ml volume using water.

Effect of monomer (Acrylamide) concentration:

The monomer concentration increases the %G and %GE increases at the initial stage and with further increase of monomer concentration it decreases. This is mainly due to the formation of homopolymer of AAM at the higher concentration.

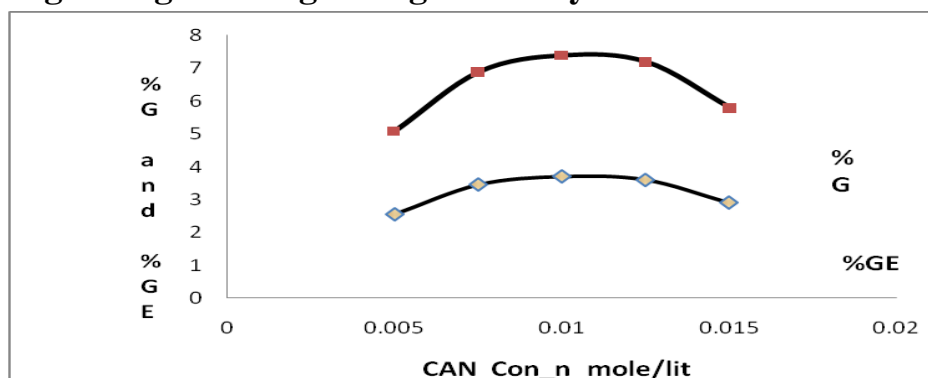
monomer (Acrylamide) concentration versus % grafting



➤ **Effect of Initiator (CAN) (Ceric ammonium nitrate) concentration:**

The effect of the concentration of initiator Ce^{4+} (ceric ammonium nitrate) on grafting AAm (Acrylamide) onto patanwadi wool. By keeping constant all the variables, the amount of CAN used was varied. It was observed that with increasing the initiator concentration the percentage of grafting as well as the initial stages and with further increase of initiator the graft percentage as well as the grafting efficiency decreases dramatically. This may be due to the fact that with high concentration of the initiator more and more homopolymers are formed thereby decreasing both %G and %GE.

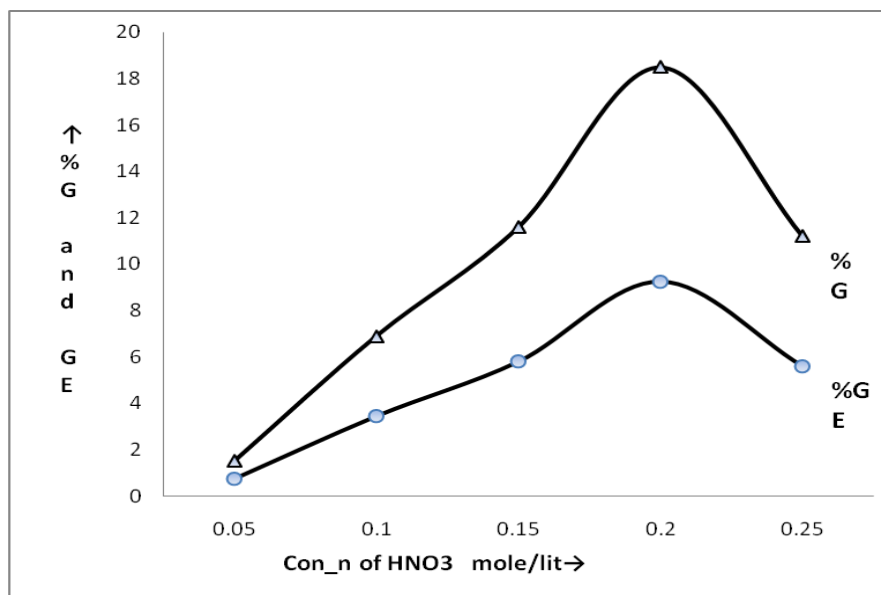
Initiator(CAN)(Ceric ammonium nitrate) concentration versus %grafting and % grafting efficiency



➤ **Effect of HNO₃ concentration:**

The nitric acid (HNO₃) concentration increases the % G and % grafting efficiency increases at the initial stages and with further increase of HNO₃ concentration it decreases.

HNO₃ concentration versus % grafting, % grafting efficiency



The role of nitric acid in wool grafting is readily understood if we assume the mechanism shown



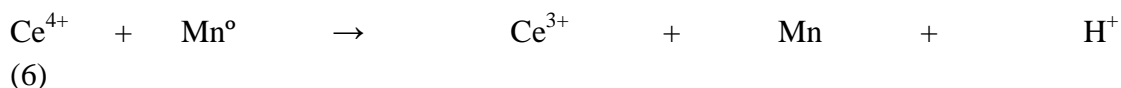
Ceric ion in water is believed to react as shown in eqs. (4) and (5).



Ceric ion exists as Ce⁴⁺, [Ce(OH)₃]³⁺ and [Ce-O-Ce]⁶⁺ in water solution. The observed zero grafting at zero nitric acid concentration indicates the inability of [Ce-O-Ce]⁶⁺ to form complex with wool (WH).

The percentage and efficiency of grafting increase with increase in [H]⁺. This is attributed to increases in the concentrations of [Ce(OH)₃]³⁺ and (Ce)⁴⁺ at the expense of [Ce-O-Ce]⁶⁺, Ceric (Ce)⁴⁺ and [Ce(OH)₃]³⁺, being smaller in size, are more effective in their ability to form complexes with wool than [Ce-O-Ce]⁶⁺. With further increase in nitric acid concentration beyond 0.15M, it was observed that efficiency of grafting decreases. This is explained by the fact that as [H]⁺ increases, the equilibria

(4) and (5) shift towards formation of more and more $(\text{Ce})^{4+}$ and $[\text{Ce}(\text{OH})_3]^{3+}$. These species at higher concentration affect the grafting adversely. Instead of propagating the polymeric chain, these species at higher concentration affect the termination steps, thus lowering the efficiency of grafting. Moreover, ceric ion has been reported to be involved in oxidative termination³² of growing monomeric chain as shown in eq. (6).

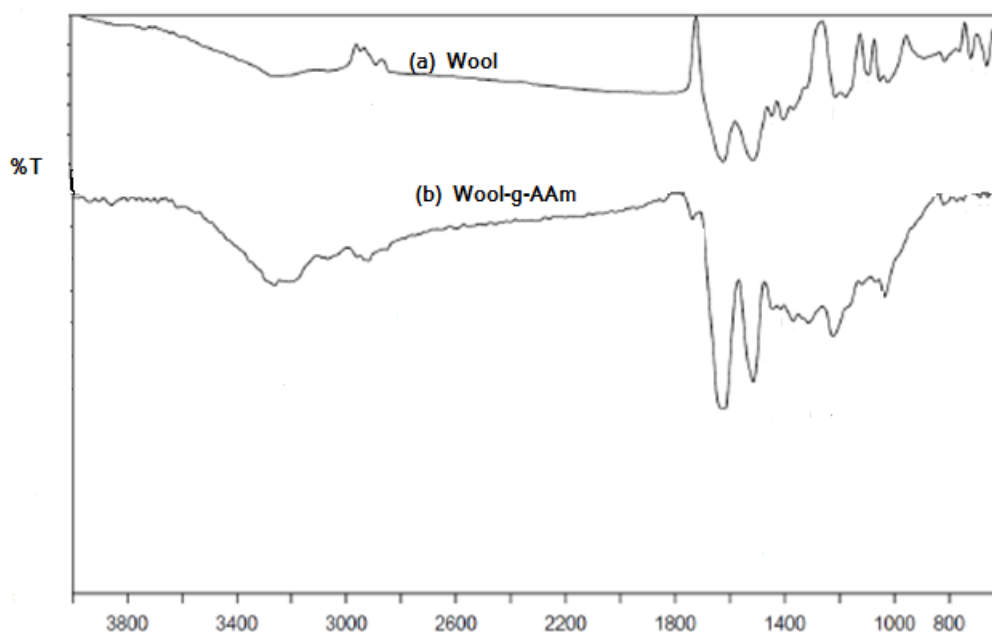


The present study indicates that in ceric ion-initiated grafting, nitric acid (0.15-0.20M) plays a definite role in promoting grafting of poly (Acrylamide) onto wool.

➤ Conformation of Grafting:

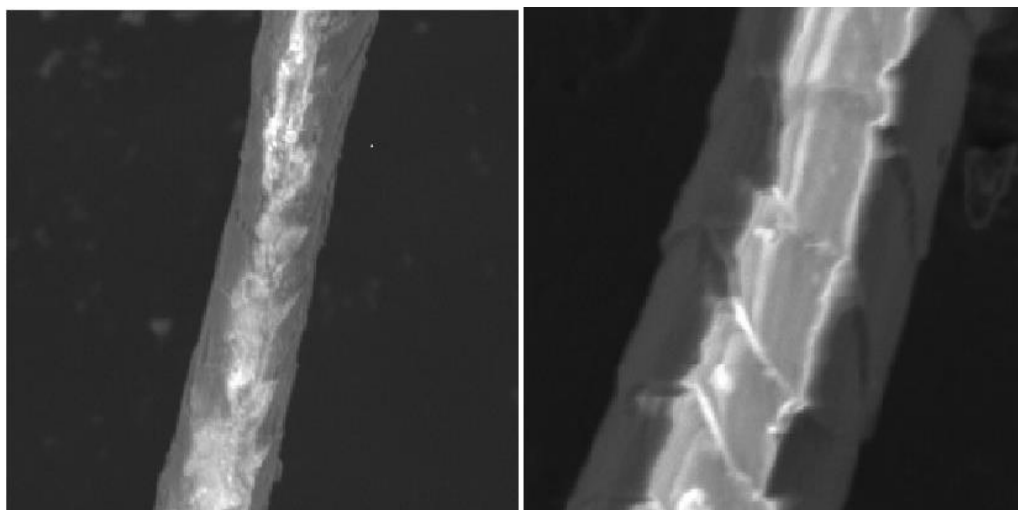
- **FTIR(Fourier Transform Infrared Spectroscopy):**

FTIR spectra of Purified Patanwadi wool and Wool-g-AAM were obtained Spectrophotometer. I.R.spectra of the Purified Patanwadi wool, Wool-g-AAM were compared. Peaks at 1737 cm^{-1} due to $>\text{C} = \text{O}$ is observed due to grafted poly(AAm).



FTIR of (a) Pure Wool and (b) Wool-g-AAM

➤ **SEM(Scanning Electron Microscopy):**



**Purified Patanwadi wool
SEM(Fig.III)**

**Wool-g-AAm
SEM(Fig.IV)**

Scanning Electron Micrographs of Purified Patanwadi Wool and Wool-g-AAm. samples are represented in Fig.III. to IV respectively. It appears from the SEM of purified patanwadi wool [Fig.III] sample that it has got smooth surface but upon comparing the SEM of the grafted samples it is clearly evident that a profound morphological changes have taken place because of ceric-induced grafting of acrylamide onto Patanwadi wool. Depending upon the nature of the individual monomer used for grafting onto patanwadi wool, the topology is dictated by them: lumpy morphology is observed in the case of AAm [Fig. IV].

➤ **WRV(Water Retention value):**

Water retention value of Acrylamide grafted Patanwadi wool fiber.

| Sample Name | % grafting | WRV |
|-------------------------|------------|-----|
| Purified patanwadi wool | - | 24 |
| Wool-g-AAm(GW 32) | 2.1 | 32 |
| RGW-2 | 4.4 | 34 |
| GW-11 | 5.1 | 40 |
| GW-9 | 6.5 | 44 |
| GW-13 | 7.4 | 46 |
| RGW-1 | 11.6 | 50 |
| GW -19 | 18.5 | 54 |

Conclusion:

Patanwadi wool has been grafted with AAM initiated by tetravalent ceric ion. The effect of monomer Concentration, initiator Concentration, nitric acid concentration on graft yield have been reported. With increasing the concentration of the monomer as well as the initiator the graft yield decreases due to the formation of homopolymer formation. This is obvious since ceric ion is a very good oxidizing agent with very high oxidation potential and it interact with AAM forming the homopolymer rather than the graft copolymer at higher concentrations. The evidence of grafting has been ascertained from the WRV, FTIR spectra and the morphology has been noted from the SEM figure. Grafting products show improved water retainion values of Patanwadi wool fibre.

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